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Microprobe analysis of the corroded surface of a silicate glass

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A soda lime silicate sheet glass was corroded in acid (pH = 0) and alkaline (pH = 11) aqueous solutions at 30 ± 1° C for various lengths of time. The concentration profile of CaO and SiO_2 within the leached layer was estimated with electron microprobe analysis. Formation of a silica rich layer at a depth of about 10 μm from the bare surface followed by a calcium rich layer, which again in some cases is followed by silica rich and calcium rich layers, were observed. The number and intensity of these layers changed with the pH value of the corroding solution, and at the same pH value changed with time of leaching.

1. Introduction

When a piece of ordinary silicate glass is brought in contact with neutral or acidic aqueous solutions, alkali ions are extracted into the solution in preference to silica and an alkali deficient leached layer is formed on the surface of the virgin glass. The formation of this layer usually reduces the rate of alkali extraction by forming a barrier through which further alkali ions must diffuse before they can be brought into solution. The thickness of the silica-rich films and probably also their compactness varies with the composition of the glass, and for the same glass depends on the test conditions, time, temperature and pH of the solution. Under identical conditions of corrosion, a low durability glass usually produces a thicker film than a high durability glass [1].

Binary alkali silicate glasses are completely hydrolysed by aqueous solutions. Substitution of CaO for SiO_2 in binary alkali silicate glass increases durability. This phenomenon is puzzling and not properly understood particularly when CaO is very much less stable in neutral or acidic aqueous solutions than SiO_2. From a complete chemical analysis of the leach solution used to corrode soda limesilicate glass it is known that the amount of CaO extracted by water is less than that expected if it had been removed as a result of network breakdown of the silica structure [2]. Possible explanations for this phenomenon are that calcium, released by the glass through network breakdown, is partly retained by the leached layer through absorption/compound formation, or that silica is preferentially extracted from the bulk of the leached layer formed on the surface of the glass leaving it with a CaO/SiO_2 ratio higher than that of the original glass. However, as pointed out earlier the second suggestion is contrary to thermodynamic expectation for CaO in neutral water is very much less stable than SiO_2.

Wikby [3], while studying the electrical resistance of corroded surface at different depths of a commercial glass electrode, observed the existence of a highly resistive layer within the leached layer, and not at the extreme bare surface of the leached layer, where SiO_2 concentraction is expected to be maximum. To understand the corrosion mechanism of soda lime silicate glass by aqueous solution, in the present investigation we have studied the concentration profile of CaO and SiO_2 in the leached layer formed on the surface of a sheet glass after immersion (for different lengths of time) in aqueous solutions buffered at two different pH values.

2. Experimental and results

A commercial sheet glass (chemical composition given in Table I) was cut into pieces (8 × 5 × 2 mm) and repeatedly washed with acetone and distilled water to make the surfaces clean. The surface adherent water was wiped off with clean soft tissue paper and the pieces stored in a desiccator.

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TABLE I Composition of the glass (wt %)

SiO_2	CaO	MgO	Al_2O_3	Na_2O
72.7	8.3	2.1	1.3	15.5

Two solutions of pH values 0 and 11 were made. The glass pieces were immersed in these solutions for various lengths of time from 1 to 24 h at 30 ± 1° C. After the required time of immersion the glass piece was taken out, the adherent liquid on the surface was soaked away with fine grained filter papers. The corroded piece of glass was then cut into two pieces along the axis perpendicular to the original flame polished surface, and mounted on a sample holder with araldite. The freshly cut surface was initially polished with −800 mesh ignited Al_2O_3 powder followed by diamond paste lapping to a ninth class finish. The polished surface was coated with carbon along with the standard (Wallstonite) to obtain a stablized integrated sample current with 0.1 μA with a drift of less than 0.1%. The counting times were varied to achieve a total count of 10^5 impulses for each data point for a statistical error of less than 0.6% [7]. Some typical concentration profiles of CaO and SiO_2 within the leached layer are shown in Figs. 1

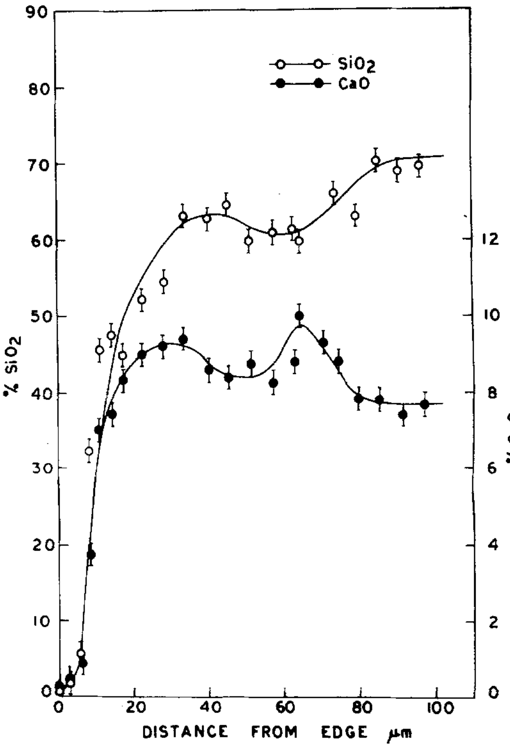

Figure 2 Concentration profile of SiO_2 and CaO in the leached layer after 24 hours at pH = 0.

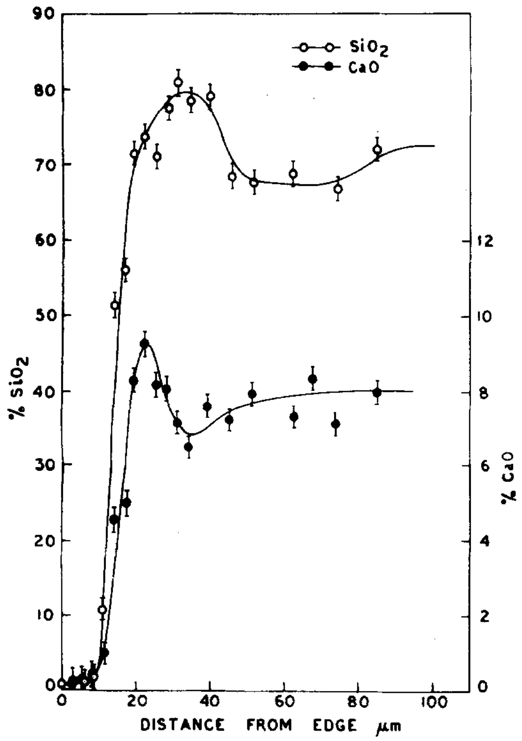

Figure 1 Concentration profile of SiO_2 and CaO in the leached layer after 8 hours at pH = 0.

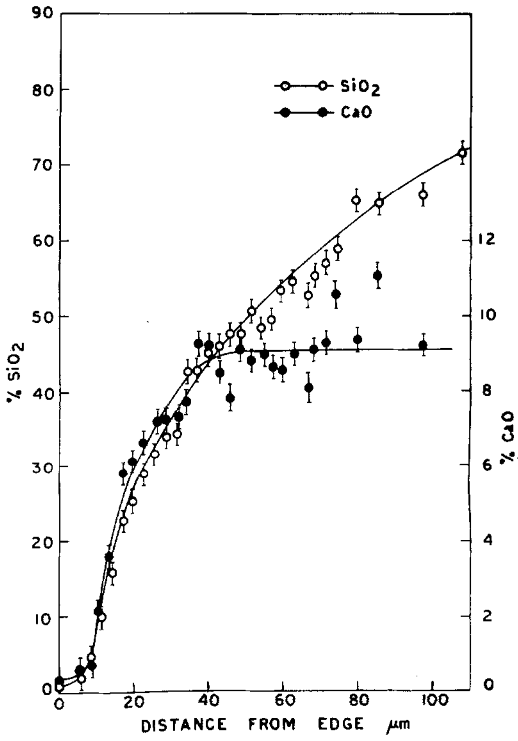

Figure 3 Concentration profile of SiO_2 and CaO in the leached layer after 24 hours at pH = 11.

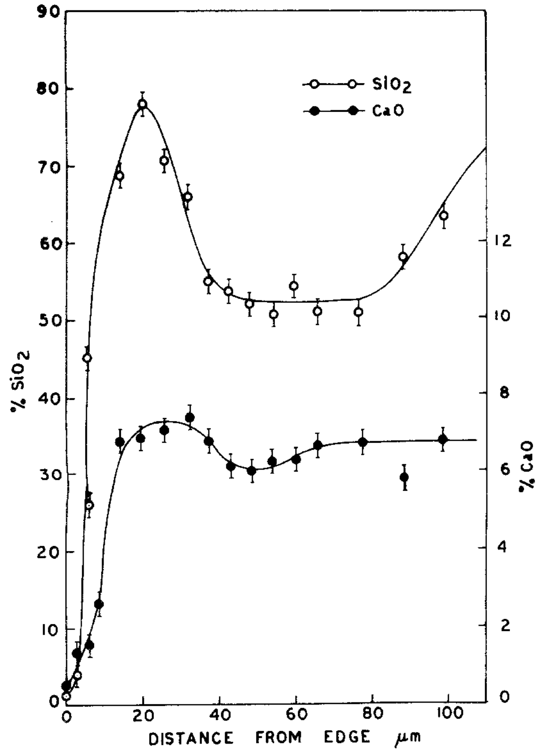

Figure 4 Concentration profile of SiO_2 and CaO in the uncorroded glass at different depths from the surface.

to 3. Fig. 4 gives the measured concentration profile of an uncorroded virgin glass. The graphs show the most representative data among at least 3 scans. In most of the cases the scatter of individual points among 3 runs was around 10%. The analysis was carried out by a step scanning procedure taking point count data for every 2.85 μm shift from the edge. Each alternative data point was started with Ca (Kα) and Si (Kα) and the intensities were measured by changing the Bragg angle only.

3. Discussion

The corrosion of soda limesilicate glass by aqueous solutions can be qualitatively described in terms of the following chemical reactions :

(a) the penetrations of proton (probably hydrated) from water into the glassy network, replacing the sodium ion into solution,

$$\rightarrow Si{-}O^-Na^+ + H_2O \rightleftharpoons \rightarrow Si{-}OH + Na^+ + OH^-$$

(b) the hydroxyl ion in solution disrupts siloxane bond in glass,

$$\rightarrow Si{-}O{-}Si \leftarrow + OH^- \rightleftharpoons \rightarrow Si{-}OH + \rightarrow Si{-}O^-$$

(c) the non-bridging oxygen formed in the above reaction reacts with further molecule of water producing hydroxyl ion, which repeats the reaction (b) again,

$$\rightarrow Si{-}O^- + H_2O \rightleftharpoons \rightarrow Si{-}OH + OH^-$$

Since solubility of SiO_2 in neutral or acidic aqueous solution is very small [4], from the above equations it is clear that in acidic solution (pH = 0 in the present investigation) sodium and calcium ions will be extracted from the glass surface, and a silica rich layer will be formed. If during leaching the incoming protons, on average, occupy the same space as previously occupied by the alkali and alkaline earth ions, and no major change in the morphology of the silicate network occurs (i.e. compaction or swelling of the leached layer) then after leaching the concentration of silica per unit volume will not change. Due to extreme mobility of sodium ions in silicate glass its concentration cannot be measured satisfactorily with electron microprobe. From previous investigation it is known that in acid solution extraction of calcium from glass is very small, and sometimes even below the detection limit (less than 0.2 ppm) [5]. Thus a relative measure of the ratio SiO_2/CaO

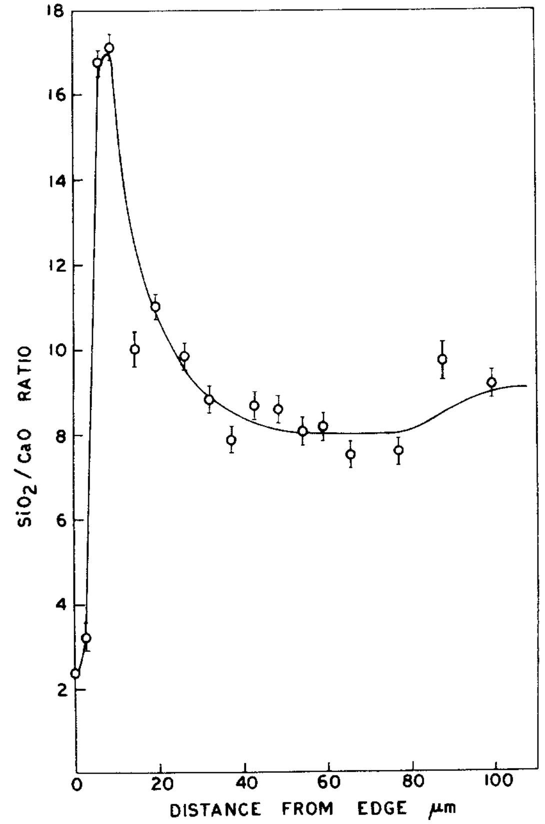

Figure 5 SiO_2/CaO ratio in the uncorroded glass at different depths from the surface.

at different depths of the leached layer is expected to throw light onto the mechanism of corrosion inhibition produced by CaO in silicate glasses.

In the present investigation the Electron Microprobe Analyser used had a beam diameter of about 1 μm. The spatial resolution under this condition, taking a density value of 3 for glass, is approximately 4 μm. Thus while scanning near the outside surface of the sample, only a part of the beam was focussed on the glass surface and this produced the artificial (fictitious) slope of the measured concentration profiles (Figs. 1 to 4). Consequently no quantitative meaning can be assigned to the silica and calcium oxide results shown in Figs. 1 to 4. However, the calculated ratio, SiO_2/CaO, as shown in Figs. 5 to 7 is free from this uncertainty for during scanning the same amount of surface area was under focus for both CaO and SiO_2.

The ratio, SiO_2/CaO on the uncorroded glass surface is shown in Fig. 5. As expected a highly silica-rich layer of about 10 μm thickness has been formed on the very outside surface of the glass. The SiO_2/CaO ratio at the peak of this silica-rich layer reached as high as 17 whereas that in the bulk glass is only 9. This type of alkali and alkaline earth depletion from the bare surface of glass in contact with moist air is a common feature and is well known [6]. Figs. 6a and b show the SiO_2/CaO ratio in the leached layer corroded in 1M HCl for 8 and 24 h respectively. In the case of 8 h corrosion, two silica-rich zones distinctly separated by a calcium oxide-rich zone (shown shaded in Fig. 6a) is evident. The first silica-rich layer (A) is of almost the same width and at the same depth from the bare surface as that found on the virgin glass. As silica (probably hydrated silica) is not significantly corroded by dilute HCl solution [4], layer A in Fig. 6a probably has the same origin as the silica-rich layer found on the surface of the virgin glass. The calcium-rich layer probably is the highly electrical resistive layer as reported by Wikby [3], its thickness, though difficult to estimate due to overlapping nature of the layers and partly due to large beam area of the Electron Microprobe Analyser (about 4 μm), seems to be of the same order of magnitude as that of silica-rich layer (A). It is probable that this calcium-rich layer has been formed by migration of calcium from the

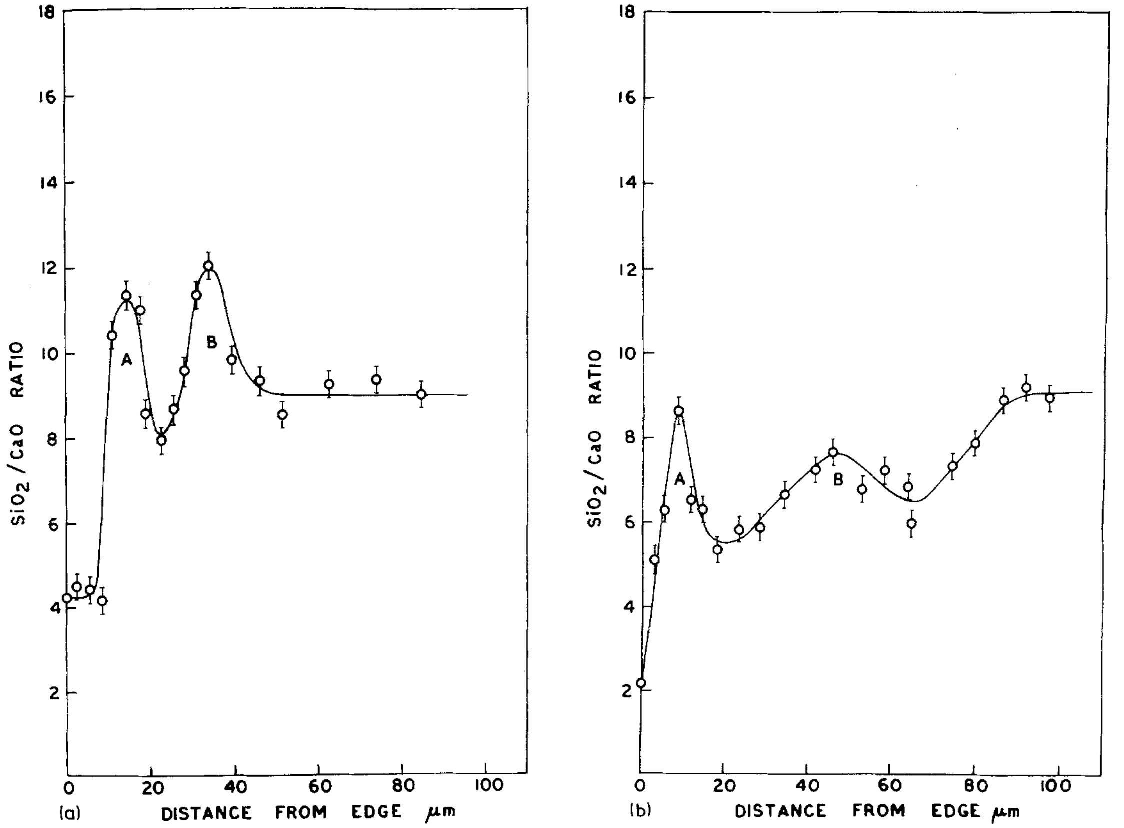

Figure 6 (a) SiO_2/CaO ratio in the leached layer after 8 h at pH = 0, (b) SiO_2/CaO ratio in the leached layer after 24 h at pH = 0.

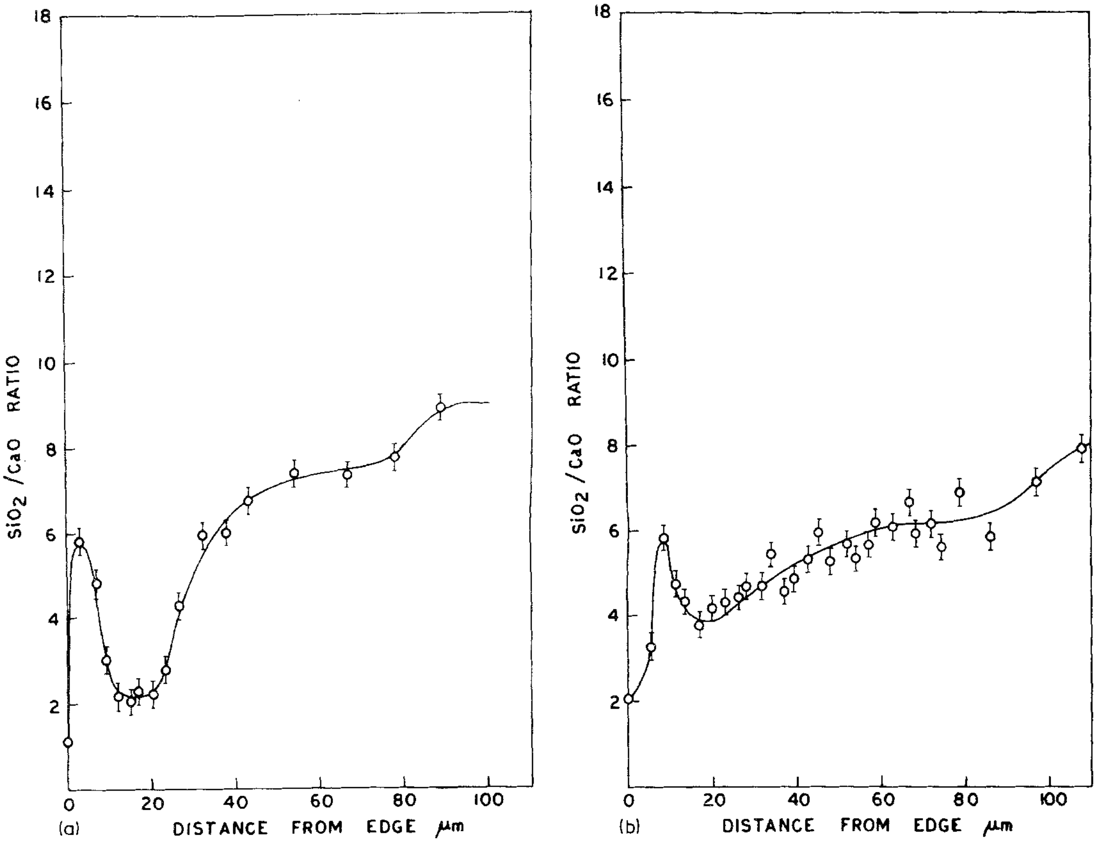

Figure 7 (a) SiO_2/CaO ratio in the leached layer after 8 h at pH = 11, (b) SiO_2/CaO ratio in the leached layer after 24 h at pH = 11.

inner side of the leached layer, and correspondingly a higher SiO_2/CaO layer has been formed, (B), on the other side of the calcium-rich layer. Under present experimental set up the depth of corrosion is about 50 μm after 8 h of leaching.

The results of Fig. 6b (24 h corrosion) is qualitatively similar to that of Fig. 6a. However, there is a significant difference in the quantitative nature of these two curves. In Fig. 6b the same silica-rich layer, (A), is observed practically at the same depth of corrosion, and the layer is also of almost same thickness. This is followed by a calcium-rich layer which again is followed by a silica-rich layer, (B), as in Fig. 6a. However, layer, (B), after 24 h leaching is followed by a second calcium-rich layer which is apparently absent after 8 h leaching. The total depth of corrosion is about 90 μm and nowhere within the leached layer is the SiO_2/CaO ratio raised more than that of the virgin glass (9). From these results it appears that after a long time of corrosion in acidic aqueous solution, a number of calcium-rich layers are formed within the leached layer, and the mechanism of glass corrosion, even under identical conditions of corrosion, changes with time.

Figs. 7a and b show the results of corrosion at pH value 11 after 8 and 24 h respectively. Hydrated silica is unstable at pH $\geqslant$ 9 [4]. In alkaline medium, ionization of silicic acid takes place with consequent breakdown of the silica network: In spite of rapid silica dissolution, a relatively silica-rich layer (although of much smaller magnitude than in acid solution) is apparent at both the times in alkaline solution. The lime-rich layer within the leached layers is very broad, and the relative depth of corrosion is considerably more at pH 11 than at pH 0 with corresponding time after 8 h at pH 11, a very broad second silica-rich peak, (B), occurs at 40 to 50 μm depth. However, after 24 h of leaching the existence of this second peak could not be discerned from the present study.

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